

MECHANISMS, MODELS, AND MYTHS: FICTION AND FACT IN TROPOSPHERIC CHEMISTRY*

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INTRODUCTION

During the last 5 to 10 years, modeling of the chemistry of the lower and the upper atmosphere has become popular, not only from the viewpoint of basic science but also as a basis for pollution control strategies in both regions of the atmosphere. Thus, significant progress has been made in taking complex kinetic and mechanistic information and, by use of modern computers and associated mathematical methodologies, developing submodels of chemical transformations in the troposphere. These are then incorporated into a variety of overall airshed models.

Properly understood and utilized, that is, with a clear understanding of both their usefulness and their limitations, airshed models describing, for example, ozone formation from its precursors (hydrocarbons (HC) and oxides of nitrogen (NO_x)) during transport and transformation across an air basin, can be helpful tools to those responsible for the control of this secondary pollutant. Indeed, such models are currently being used by the U.S. Environmental Protection Agency (EPA) as a major element of their proposed revised oxidant control strategies.

While it is exciting for most scientists to see how fundamental data on reaction kinetics and mechanisms are now being put to use in solving real-world problems, it is also somewhat sobering to realize that billions of dollars ride on the results that are being derived from such models. Entire industries are seriously affected by the accuracy of model predictions; consider, for example, the aircraft and fluorocarbon industries in relationship to the ozonosphere question. Although less dramatic in public visibility, these increasingly stringent tropospheric oxidant controls being proposed and implemented for seriously polluted air basins also have significant economic ramifications, not only for automobile manufacturers but also for such stationary sources of reactive organics as coal-fired power plants, the paint industry, and so forth.

Thus, while acknowledging the importance and usefulness of such chemical kinetic computer models, it seems useful to pause and examine those factors that significantly affect their accuracy and precision. In so doing, remember

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that a chemical model describing "Los Angeles smog," for example, really consists basically of a photochemical reaction mechanism plus a computer.

Historically, in the early days of gas-phase photochemistry and photooxidation, the validity of the kinetic-mechanistic "models" developed for even very simple systems was limited to a significant extent by mathematical capabilities. Thus, obtaining mathematical solutions describing the events occurring in even relatively uncomplicated chain reactions was at best very tedious; the generation of reliable time-concentration profiles for reactants and products in more complex systems was virtually impossible. Sometime around the late 1950's and early 1960's, the power of computer technology and the associated mathematics began to emerge, and during the last 15 years, the computational aspects of chemical models for multicomponent simulated atmospheres have generally not been the limiting factor in the final accuracy of the model's predictions. Present computers are, of course, highly sophisticated and capable of handling what to a photochemist of the 1950's would have been an incredible number of individual reactions, for example, well over 200 in the propylene-NO_x-air-hν system alone! Thus, today kinetic computer models are, in effect, chemistry limited; that is, the validity of these models describing reaction sequences in the natural or polluted troposphere depends far more on the accuracy and precision of the input chemical data than upon the mathematical subtleties and techniques presently used to translate such data into useful concentration-time profiles.

Experienced atmospheric chemists are usually aware of the deficiencies in the experimental data base for both the troposphere and the stratosphere and generally assign realistic probable errors to the predictions produced by their models of chemical transformations. This is important because only in this way can one who is not an expert in this specific field have some understanding of the degree of accuracy and precision of models used in control strategies. Unfortunately, some scientists who develop and utilize photochemical models for tropospheric pollution do not always clarify the degree to which the experimental data that they are using in their models are reliable, both in accuracy and precision. Thus a nonchemist modeler could unknowingly generate an overall airshed model quite sound in one component, for example, in the submodel dealing with meteorology, but seriously in error in the package describing the chemical and physical transformations of pollutants during transport in the real atmosphere.

This paper will illustrate some aspects of this general problem, that is, the dangers inherent in being overconfident about the reliability (especially the absolute accuracy) of the atmospheric chemistry input into current models for tropospheric air pollution. First, a review is presented of the criteria that must be met before even a simple homogeneous gas-phase photochemical reaction carried out under laboratory conditions can be considered proof of a mechanism. Then, the paper will discuss specific examples of "fiction and fact" in the enormously complex heterogeneous systems that characterize ambient polluted atmospheres.

In so doing, the author will express his personal ideas on the subject. Thus, no attempt will be made to review or reference the literature; this has been done elsewhere (refs. 1 to 3). Furthermore, the examples cited will be

taken largely from current work, much as yet unpublished, in the laboratories of the University of California Statewide Air Pollution Research Center and Departments of Chemistry and Biology.¹

CRITERIA FOR ESTABLISHING THE VALIDITY OF A MECHANISM FOR

A GAS-PHASE PHOTOCHEMICAL REACTION

Some of the more important types of experiments that should be carried out in the laboratory to develop and validate a mechanism for a gas-phase photochemical process are summarized below; they are discussed in detail elsewhere (ref. 4):

- (1) Measurement of the primary (ϕ) and overall (Φ) photochemical quantum yields for the loss of reactants
- (2) Identification and determination of ϕ and Φ for the formation of major and minor products
- (3) Identification and quantification of trace, but mechanistically important, product molecules
- (4) Identification and measurement of the concentration-time profiles of key intermediate species, for example, methyl or hydroxyl radicals, singlet molecular oxygen ($O_2^1\Delta$), triplet states of photoexcited organic compounds, and unstable isomeric forms
- (5) Determination of the quantum yields of the photophysical processes associated with the absorption of light, for example, internal conversion, intersystem crossing, fluorescence, and phosphorescence

In the laboratory, insofar as possible, all of these experiments should be conducted as a function of temperature, wavelength and intensity of absorbed radiation, pressures and/or concentrations of reactants, physical and chemical quenching by added gases, surface/volume ratio, other parameters that involve the homogeneous versus heterogeneous nature of the reaction, and when appropriate, pressures of gaseous free radical traps (e.g., I_2 , NO, and olefins). Additionally, isotopic labeling experiments may be required for confirmation. Finally, a reasonably good material balance (number of atoms in reactant molecules equal to number of atoms in product molecules) should be sought.

Considering the number and complexity of such experiments required to elucidate with confidence the mechanism of the gas-phase photooxidation of

¹The author's colleagues have tackled a variety of difficult research problems in tropospheric chemistry with zeal and competence to produce the results discussed herein. They include W. L. Belser, Jr., R. Atkinson, K. R. Darnall, R. A. Graham, D. Grosjean, G. B. Knudson, R. Perry, J. P. Schmid, J. P. Smith, E. C. Tuazon, K. A. Van Cauwenberghe, A. M. Winer, F. R. Burleson, D. R. Fitz, P. M. Hynds, K. Pettus, and T. M. Mischke.

only a single compound, say formaldehyde or methyl ethyl ketone, one might despair at the thought of ever understanding with some degree of assurance the mechanism of photochemical smog formation in urban atmospheres. The urban atmosphere may contain literally hundreds of hydrocarbons - alkanes, alkenes, and aromatics - and other organics such as aldehydes, ketones, and halogenated species, as well as inorganics, including NO, NO₂, HONO, and HNO₃.

Actually, much progress has been made in dealing with this admittedly difficult situation, partly by studying the reactions of model hydrocarbons in simulated atmospheres contained in smog chambers. On the basis of such studies and by utilizing fundamental kinetic and mechanistic data, both highly detailed complex mechanisms (ref. 1) and simplified lumped parameter models (ref. 5) have been developed. These predict values in quite good agreement with experiments for such parameters as rates of loss of hydrocarbons, rates of formation of O₃ and peroxyacetyl nitrate (PAN), NO to NO₂ conversion, and maximum O₃ levels. However, as implied earlier in a more general context, it is the author's personal feeling that a sense of false security has developed in some quarters as to the actual ability of such models to reflect accurately the events occurring in real ambient air over wide ranges of temperature, relative humidity, intensity and wavelength of solar irradiation, and number, nature and concentration of reactants - all in a heterogeneous system where gas-to-particle conversion and associated surface reactions play a major role in determining air quality.

Therefore, over the last few years the research team at the Statewide Air Pollution Research Center (SAPRC) and the Chemistry Department at the University of California, Riverside, has developed several facilities and experimental techniques that permit exploration of the effects of changing these variables on the rates and mechanisms of formation of major, minor, and trace pollutants over a wide range of concentrations, approximately 10 ppm to 10 ppb. The following sections illustrate how these facilities have been used to test several recently expressed ideas important to modeling tropospheric reactions and how these ideas were found to be significantly in error.

SMOG CHAMBER STUDIES OF PHOTOCHEMICAL SMOG FORMATION IN

SIMULATED URBAN ATMOSPHERES

Spectroscopic Identification and Measurement of Minor and Trace Products

Having Mechanistic and Health Implications:

Establishment of a Material Balance

Two of the grave deficiencies of many of the earlier experiments on photochemical oxidant formation from HC-NO_x mixtures in smog chambers are (1) the inability to detect by conventional methods (e.g., "wet chemistry") many of the highly labile molecules produced and (2) as a consequence, an inability to achieve good (e.g., 85 to 90 percent or greater) overall material balances for nitrogen and carbon, indicating that substantial quantities of products were not being identified. Obviously, at best this lack of crucial product information

frustrates those attempting to develop reliable mechanisms for the photooxidation of various HC-NO_x systems; in practice, the problem becomes critical when smog chamber results with such information gaps are used without considerable caution in developing computer kinetic models of photochemical smog.

The short scan times, large wave number range per scan, and high spectral resolution and sensitivity of long-path (50 to 1000 m) Fourier transform infrared (FT-IR) spectrometers make them highly useful tools for determining time-concentration profiles for a large number of reactive species that cannot be measured by conventional monitoring instruments. Furthermore, in situ FT-IR spectroscopy can contribute to improved nitrogen and carbon balance in chamber experiments. For example, an interferometer interfaced with a multiple-reflection cell in the SAPRC 5800-liter evacuable smog chamber (fig. 1) was used to measure spectra during an experiment in which a mixture of propylene, NO, and NO₂ (at concentrations in the ppm range) in air at 9.4° C was irradiated with a 24-kW solar simulator.

A high-resolution (0.125 cm⁻¹) spectrum from this run, shown in figure 2, contains quantitative information about four species not normally monitored in smog-chamber studies, nitric acid (HNO₃), peroxyxynitric acid (HOONO₂), formic acid (HCOOH), and N₂O₅, and a fifth, formaldehyde (HCHO), that is generally monitored by a notoriously unreliable wet-chemical method. The observation and quantitative determination (with a time resolution of several minutes during a multihour irradiation) of these species illustrate the increased amount of useful chemical information afforded by the FT-IR technique. In part, this has allowed much better mass balances, approaching 100 percent, to be obtained.

It is interesting that it was in similar FT-IR studies that the formation of peroxyxynitric acid was first discovered in 1976 by Niki and co-workers (ref. 6) and independently by Hanst and Gay (ref. 7). Until that time the generation of peroxyxynitric acid under atmospheric conditions generally had not been anticipated. Formation of HOONO₂ by reaction of HO₂ with NO₂ in photochemical smog (as well as in the stratosphere) is plausible both thermodynamically and kinetically. However, while the rate of formation of HOONO₂ in such systems could be as large as that of peroxyacetyl nitrate (PAN), it is less stable thermally. Thus, only low concentrations of HOONO₂, relative to PAN, should be expected under warm, ambient conditions. However, the discovery in the laboratory of HOONO₂ by FT-IR spectroscopy has spurred a search for it in ambient air, especially on cooler days in bright sunlight.

Effects of Temperature on Ozone Formation

One of the long-term myths about photochemical smog is based in part on statistical analysis of air quality data in the Los Angeles Air Basin. Essentially, the myth is that ozone formation is negligible at temperatures below 13° C; indeed this statement was made in a recent draft of the revised EPA document, "Air Quality Criteria for Photochemical Oxidants."

In order to examine the validity of this statement and to test current models of photochemical smog which are based to a large degree on smog chamber data taken at typical chamber operating temperatures (20° to 30° C), the SAPRC

research team recently initiated a series of experiments on HC-NO_x mixtures in air over a wide temperature range (5° to 50° C) in the thermostatted, evacuable chamber (fig. 1). Preliminary results are interesting and informative.

First, in a mixture of a HC surrogate (2.3 ppm of carbon) and NO_x (0.24 ppm) at 5° C, enough O₃ was generated to exceed the Federal ambient air quality standard for oxidant, 0.08 ppm for 1 hour. This seems to refute the statement cited at the beginning of this section, especially when taken with the recent observation that significant levels of O₃ can build up on bright and cold winter days in Denver.

Second, in a run at 49° C two especially interesting features of the O₃ time-concentration profiles were observed: not only did the ozone maximum occur after complete consumption of the NO_x initially present (and plateau at the peak for over 1 hour), but also there were two ozone maxima. To the author's knowledge, this is the first time that such phenomena have been observed in smog chamber studies. Thus, although in these runs the HC and NO_x concentrations were in the ppm range and it remains to be seen whether these phenomena also occur at concentration levels in the ambient range, it is abundantly clear that the atmospheric chemistry of the polluted troposphere is significantly dependent on temperature. Although this can be deduced from an examination of the temperature dependencies of certain key elementary reactions in current models, for example, the temperature coefficient of the rate of dissociation of PAN,



obviously a great deal of experimental work must be carried out in the future to obtain specific, accurate information on this important, real-world concern: What is the effect of temperature on photochemical oxidants?

AMBIENT AIR STUDIES OF PHOTOCHEMICAL SMOG

Identification of Trace Pollutants

In order to obtain a comprehensive understanding of chemical and physical transformations in the polluted troposphere so that one can validate kinetic computer models (and better estimate the possible impact of photochemical smog on health), conventional air monitoring instrumentation must be augmented by sensitive and specific analytical methods for trace species. For the past 25 years, long-path infrared (LP-IR) absorption spectroscopy has played an important role in the identification and quantitative determination of such trace pollutants, not only in chambers (*vide supra*) but also in ambient air. Two examples are the discovery and identification of PAN in photochemical smog some 20 years ago by Stephens and associates (ref. 8) and the FT-IR study of ambient smog by Hanst and associates of the EPA in Pasadena, California, in the summer of 1973 (ref. 9).

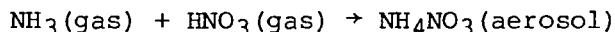
In collaboration with Hanst, who designed and furnished the basic instrument, another long-path Fourier transform infrared facility (in addition to that

associated with the evacuable chamber, vide supra) was established at SAPRC in the summer of 1976. The prime task was to employ this system to identify and measure trace species in the ppb to ppm (parts per hundred million) concentration range in ambient atmospheres. The design and operation of this FT-IR facility and some of the initial results obtained with it are summarized here and presented in more detail elsewhere (ref. 10).

In this system, a Fourier transform infrared spectrometer has been interfaced with a multiple-reflection cell consisting of eight gold-coated mirrors with a 22.5-m base path (fig. 3). This cell has been routinely operated at total path lengths of 1 km or greater, and detection limits of 2 to 10 ppb have been established for many species suspected or known to be present in photochemical smog. These include HCHO, HCOOH, HNO₃, HONO, NH₃, N₂O₅, PAN, and other peroxyacyl nitrates. Some of these are shown in table I (refs. 9 and 11 to 15), along with the useful measurement frequencies and the absorptivities (as well as the resolutions at which they were measured).

During the summer of 1976 the first spectroscopic detection of HNO₃ and HCHO in ambient smog was achieved and time-concentration profiles were obtained for these species as well as for formic acid, ammonia, ozone, and PAN (ref. 10). Concentrations of a number of these trace species detected during a smog episode in Riverside, California, on August 12, 1977, as determined with this FT-IR facility operating at a path length of 900 m, are shown in table II. Of particular interest is the fact that substantial levels of the basic NH₃ and the acidic HNO₃ can coexist in ambient smog, as seen from the spectra taken at 12:32 (fig. 4).

Clearly, much research lies ahead in order to understand better the obviously complex interactions in the heterogeneous system,



Indeed, such an understanding may well be essential in determining the extent and causes of a so-called nitrate filter artifact that has been reported recently by several laboratories. Thus, in the past, using conventional high volume samplers and glass fiber filters, particulate nitrate levels as high as 80 µg/m³ on some winter days have been reported at a number of monitoring stations throughout California's South Coast Air Basin. However, Spicer et al. have presented considerable evidence that much of this nitrate that has been assumed to be particulate in origin actually may result from gaseous nitric acid being neutralized on the glass filter (ref. 16). There seems to be a problem here, and current research is going on in a number of laboratories to define its nature and magnitude.

Another species of considerable interest in terms of its mechanistic importance is hydrogen peroxide. In photochemical smog, it is formed in a chain termination reaction and, indeed, is an index of hydroperoxyl (HO₂) radical concentrations. Thus, knowledge of the concentration of H₂O₂ in simulated atmospheric systems and actual urban smog is particularly interesting to atmospheric modelers. However, because of the analytical difficulties encountered in measurements of ppb concentrations of H₂O₂, there have been relatively few laboratory or smog chamber studies in which its levels were

monitored quantitatively, or even qualitatively. Furthermore, there has been only one set of atmospheric measurements, that of Gay and Bufalini (ref. 17). These workers reported H_2O_2 concentrations of up to 40 ppb in Hoboken, New Jersey, and of up to 180 ppb in Riverside, California, in 1970 during a very severe smog episode in which the oxidant concentration reached 0.65 ppm.

Recently SAPRC collaborated with Kok and co-workers at Harvey Mudd College and Gay from the EPA Research Triangle Park Laboratory in measurements of hydrogen peroxide concentrations at two locations (Claremont and Riverside) in California's South Coast Air Basin during the months of July and August 1977. Three different analytical methods were employed: a chemiluminescent method and two colorimetric procedures.

There was reasonable agreement among the three procedures, and typical midafternoon concentrations of H_2O_2 during moderate smog episodes (i.e., O_3 concentrations of ≈ 150 to 220 ppb) ranged from approximately 10 to 30 ppb. These values are much lower than the 180 ppb reported by Gay and Bufalini in the 1970 study in Riverside. Hopefully, predictions of ambient H_2O_2 levels generated from current chemical computer models will be consistent with these new, significantly lower values for hydrogen peroxide in ambient air.

Chemical Inhibition of Photochemical Smog

Recently, a proposal for controlling the products of photochemical smog such as O_3 , PAN, and secondary aerosols by adding to urban air 100 ppb of an inhibitor, diethylhydroxylamine (DEHA), $(\text{C}_2\text{H}_5)_2\text{NOH}$, has been strongly advocated in some quarters (ref. 18). This chemical approach, Heicklen has stated, would eliminate the need for exhaust control devices on motor vehicles and save billions of dollars. Indeed, actual field trials involving introduction of DEHA into the air of several major cities in the world suffering from photochemical smog have been suggested (ref. 19).

Heicklen's research on which his proposal was originally based was carried out on HC-NO_x systems containing DEHA at concentration levels greater than 1 ppm and was generally conducted under laboratory, not simulated ambient, conditions. Thus the researchers at SAPRC, among others, were concerned not only with the possible health effects of photooxidation products of $\text{DEHA-NO}_x\text{-HC}$ mixtures generated in ambient photochemical smog but also with the atmospheric uncertainties involved in this extrapolation (ref. 19).

To test the idea under realistic conditions, the reactions of 100 ppb and 500 ppb of DEHA in ambient air or in hydrocarbon surrogate mixtures simulating 6 to 9 a.m. Los Angeles air were studied in a large outdoor environmental chamber constructed from 2-mil Teflon² (FEP) fluorocarbon film (ref. 20), similar to the chamber shown in figure 5.

Typically, the chamber was first covered with a black plastic light shield and filled with ambient air to a volume of about 50 m³. It was then divided

²Teflon: Registered trademark of E. I. du Pont de Nemours & Co., Inc.

into two compartments of equal volume and a known amount of DEHA in high-purity N₂ was added to one of the compartments. The black cover was then removed exposing both compartments to sunlight for at least 6 hours. Since identical samples of polluted air, one with and one without DEHA, were subjected simultaneously to the same environmental conditions (i.e., solar irradiation, temperature, and humidity), differences in the time-concentration profiles of the smog parameters measured in the two compartments could unambiguously be attributed to the DEHA in one compartment.

The results for an experiment in which 100 ppb of DEHA was added to Riverside ambient air were quite revealing. The DEHA did not inhibit formation of photochemical smog; in fact, it substantially accelerated the conversion of NO to NO₂ as well as the production of O₃, PAN, and light-scattering secondary aerosols.

With 0.5 ppm of DEHA added to ambient air doped with the hydrocarbon surrogate mixture, an "intermediate" behavior was observed. Inhibition was predominant during the first hour of irradiation, but at that point a marked acceleration of smog formation took place.

In short, DEHA is indeed an inhibitor of certain symptoms of photochemical smog for several hours when present at ppm concentrations. However, it is an accelerator of O₃, PAN, and aerosol formation and NO to NO₂ conversion when present at the 100 ppb level recommended. Furthermore, even if high ppm levels of DEHA (odor threshold 0.5 ppm) could be added to ambient air (not considering the health implications, which could be serious), its dilution as the air mass was being transported would soon lead to increased photochemical smog in suburban, and even rural areas, downwind.

Clearly, proposals for the control of photochemical smog by chemical additives cannot be based only on extrapolations from experiments conducted in the laboratory at torr pressure and ppb concentration ranges. They must be experimentally validated at realistic pollutant levels in ambient air.

CHEMICAL MUTAGENS AND/OR CARCINOGENS IN REAL AND SIMULATED ATMOSPHERES

Historically, researchers and control officials have focused their attention on the criteria air pollutants - sulfur dioxide, carbon monoxide, nitrogen dioxide, photochemical oxidants (including ozone), and total suspended particulates. Recently, however, as discussed previously, considerable interest has developed in better understanding the sources, transport, and associated chemical and physical transformations and sinks of several types of "noncriteria" pollutants, including those cited in table II. Certain of these species, though present in urban atmospheres at much lower concentrations than the criteria pollutants, are known to produce disproportionately severe health effects in experimental animals, and possibly in man. A classic example is the well-known carcinogenic polycyclic aromatic hydrocarbon (PAH) benzo(a)pyrene (BaP). It is formed during the combustion of fossil fuels and in 1952 was identified and measured in ambient particulate soot particles collected at 10 stations throughout Great Britain by Waller (ref. 21). Today it is known to be distributed globally.

A second class of noncriteria pollutants of current concern are the N-nitrosamines, very potent carcinogens having the general formula R_2NNO . Recently, they have been identified in a variety of systems including pesticides, synthetic cutting and grinding fluids, and drinking water. However, in contrast to the ubiquitous nature of BaP, they have been identified as air pollutants only in a limited number of locations, including those in or near industrial plants in East Germany (ref. 22) and the United States (refs. 23 to 27). The Germany industry employed dimethylamine (DMA) and the United States plant dimethylnitrosamine (DMN) in organic syntheses.

Pronounced societal interest in such real or potential atmospheric carcinogens is illustrated by the amendments to the U.S. Clean Air Act passed by Congress and signed into law by President Carter in August 1977. Thus, Section 104(b) requires the Administrator of the U.S. Environmental Protection Agency to review and critique all available information on "nitric and nitrous acids, nitrites, nitrates, nitrosamines, and other carcinogenic and potentially carcinogenic derivatives of oxides of nitrogen." Similarly in Section 122(a), the Administrator is required to "determine whether or not emissions of polycyclic organic matter (POM) into the ambient air will cause, or contribute to air pollution which may reasonably be anticipated to endanger public health."

Clearly, these mandates reflect growing concern over possible health effects of increasing emissions of NO_x and organic particulates associated with proposed major shifts to a far greater use of coal, shale oil, diesel-powered motor vehicles, and so forth, to relieve, in part, the energy crisis facing the United States.

In terms of the thrust of this paper, fiction and fact in atmospheric chemistry, clouding the issue with respect to particulate polycyclic aromatic hydrocarbons as air pollutants are statements such as "They are chemically inert and thus are removed from the air only by rain or the slow sedimentation of the particulate." (See refs. 28 and 29.) Actually, although the evidence to date is meager, chemically speaking many PAH, including BaP, are reactive compounds in the laboratory. Thus, they might well undergo a variety of thermal and photochemical reactions in urban air with a number of copollutants; these include both molecular and radical species. (For detailed reviews, see refs. 30 and 31.)

With respect to nitrosamines, a 1976 EPA review and critique (ref. 32) states that in solution, "Unlike the secondary amines which can form nitrosamines . . . only a few tertiary amines form nitrosamines." This is clearly not the case; tertiary amines do in fact react readily in solution with aqueous nitrous acid to form N-nitrosamines (refs. 33 to 35). A key question is, "Can tertiary and secondary aliphatic amines at sub-ppm concentrations react in air with ambient levels of NO_x (containing small traces of nitrous acid)?" Thus, Hanst et al. recently showed that dimethylamine (DMA) reacts readily with HONO in air to produce dimethylnitrosamine (DMN) when both are in the ppm concentration range (ref. 36).

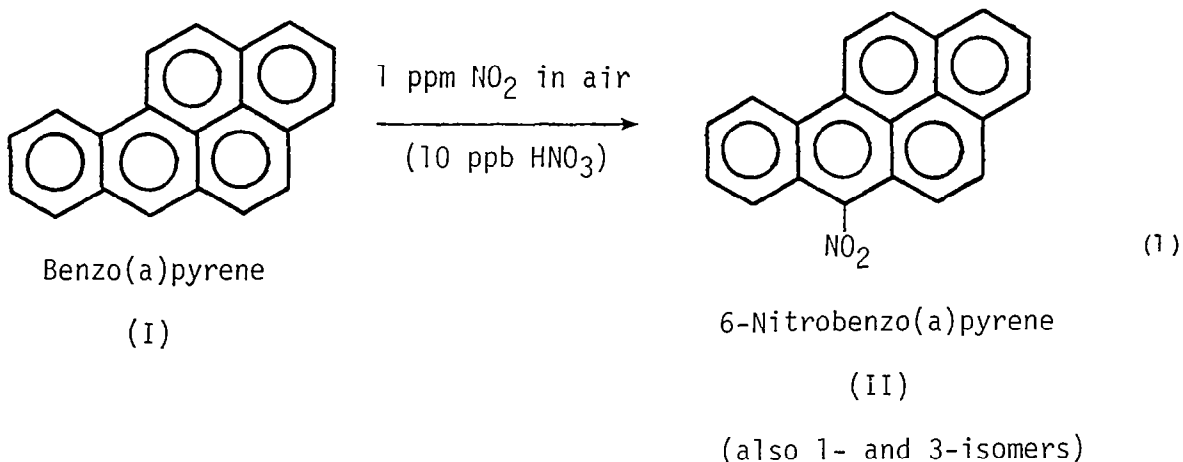
To resolve such issues involving known and potential atmospheric carcinogens, researchers at SAPRC have been studying (1) reactions in simulated and

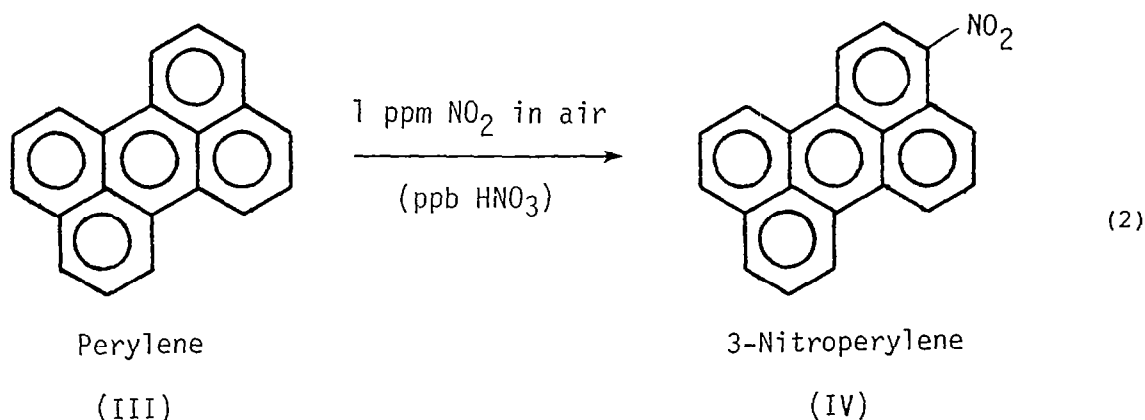
real urban atmospheres of the carcinogen BaP and of its noncarcinogenic isomer perylene and (2) reactions of mixtures of simple aliphatic amines and NO_x in air containing traces of HONO. Although at first glance the two systems, particulate PAH and gaseous nitrosamines, may seem quite unrelated, they both participate in chemical transformations in which OH and HO_2 radicals and NO_x play major roles, just as these species do in tropospheric photochemical smog and in determining the stratospheric ozone balance. For detailed considerations, the following SAPRC papers should be consulted: references 37 and 38, on the mutagenic activity of ambient organic particulates; reference 39, a recent review and discussion of the reactions of PAH and nitrosamines in simulated atmospheres which will be appearing in the Philosophical Transactions of the Royal Society; and references 40 to 41, two detailed papers on thermal and photochemical reactions in amine- NO_x -HONO-air systems.

Polycyclic Aromatic Hydrocarbons

SAPRC recently discovered direct mutagenic activity, as determined by the Ames' Salmonella typhimurium reversion microbiological assay (refs. 42 to 44) in the organic fractions of all ambient urban aerosols collected throughout southern California. This discovery led to an investigation of the reactions of BaP deposited on washed glass fiber filters with ambient photochemical smog, as well as with approximately ppm levels of O_3 , NO_2 , and PAN in simulated atmospheres. In direct contrast to the statements cited previously (refs. 28 and 29), a variety of derivatives of BaP are readily formed, including phenols, diphenols, dihydrodiols, and quinones (ref. 39).

Furthermore, in contrast to BaP which is an activatable mutagen (a promutagen) requiring microsomal activation to produce mutagenic activity, it was found that directly mutagenic nitroderivatives of BaP are readily formed upon exposure of the coated filters to 1 ppm of NO_2 in air. Additionally, it was recently found that directly mutagenic nitroderivatives are formed in a facile reaction not only from the known carcinogen BaP but also from perylene and pyrene. Both of these PAH are noncarcinogens and, along with BaP, are widely distributed in organic particulate pollutants from a variety of sources. The acid catalyzed reactions with NO_2 of BaP and perylene (deposited on filters) are as follows:





If such reactions actually occur in urban atmospheres, they may account in part for the formation of the presently unknown species responsible for the "excess" carcinogenicity (over that which could be ascribed to other known carcinogenic polycyclic aromatic compounds measured in the samples) that has been observed in animals treated with organic extracts of the particulates collected from smog and exhausts of gasoline engines (ref. 31). However, complicating matters is the fact that such gas-solid interface processes as those observed for NO_2 and the three PAH may also have occurred on the filters used to collect the particulates which were then extracted and administered to the experimental animals. Thus, the possibility of such filter artifacts must be recognized when using existing air quality data on particulate PAH to develop and validate models predicting their atmospheric levels and possible health effects (e.g., dose-response curves). Finally, there is a distinct possibility that BaP, perylene, and other PAH may react differently depending upon the physical and chemical nature of the surfaces on which they are deposited. All of these points seem relevant to atmospheric modeling of these heterogeneous processes.

Atmospheric Chemistry of Amine- NO_x Mixtures

The SAPRC research group recently studied the reactions in air of the possible atmospheric precursors to diethylnitrosamine, $(\text{C}_2\text{H}_5)_2\text{NNO}$, that is, mixtures of secondary or tertiary amines with NO_x and some HONO. Experiments were conducted both at sub-ppm levels in air in the 50 m^3 outdoor chamber shown in figure 5 (ref. 40) and at ppm levels in the long-path (720 m) FT-IR facility described earlier (fig. 3 (ref. 41)).

At sub-ppm concentrations, both diethylamine (DEA) and triethylamine (TEA) in the presence of ambient levels of NO_x (≈ 300 ppb) readily form photochemical oxidants (e.g., O_3 , PAN, and aerosols). This is seen in figure 6(a) which shows the time-concentration profiles for the loss of TEA and the formation of certain oxidant-type products. Additionally, small but significant amounts of $(\text{C}_2\text{H}_5)_2\text{NNO}$ are formed in the dark from DEA (≈ 3 percent yield) but are destroyed in sunlight. In contrast, $(\text{C}_2\text{H}_5)_2\text{NNO}$ is initially formed on irradiation of TEA- NO_x mixtures containing some HONO, reaches a maximum (≈ 1.8 percent yield), and then subsequently photodecomposes (fig. 6(b)). Thus,

in contrast to the recent EPA statement cited previously (ref. 32), under the appropriate circumstances, tertiary amines can in fact react in sunlight with air containing NO_x and HONO to form nitrosamines.

Other significant nitrogenous compounds formed in sunlight from both DEA- NO_x and TEA- NO_x mixtures include dialkyl nitramines (R_2NNO_2), which are a major product of all amines, and a number of substituted amides (fig. 6(b)). As a spin-off, dimethylnitramine ($(\text{CH}_3)_2\text{NNO}_2$) was in fact shown to be the "unknown major product" found by Hanst et al. when they irradiated dimethylnitrosamine in air (ref. 36). Finally, small amounts of acetamide (CH_3CONH_2) are present in the particulate phase from irradiation of both DEA- NO_x and TEA- NO_x mixtures.

In terms of the biological and environmental implications of these results, it is somewhat sobering to note that both $(\text{CH}_3)_2\text{NNO}_2$ and CH_3CONH_2 are carcinogens in animals, though less potent than nitrosamines; the activity of dimethylnitramine $(\text{C}_2\text{H}_5)_2\text{NNO}_2$ is not known. Furthermore, amines are emitted into industrial atmospheres as a result of a wide variety of activities; some of these are secondary and tertiary aliphatic amines or related compounds such as ethanolamines. However, although little is known about their concentrations in ambient air, they are probably usually very low. Thus, the risk of forming significant amounts of nitrosamines or nitramines in urban air from their precursors seems correspondingly small.

However, in industrial situations in which sub-ppm concentrations of amines may be released into urban atmospheres containing NO_x and HONO, within and immediately downwind from the facility, formation of significant amounts of nitrosamines in the dark and nitramines and amides in sunlight seems possible. Clearly, in such cases, measurement of the actual ambient levels of amines, NO_x , nitrosamines, nitramines, and, if possible, HONO would be useful to modelers and control officials alike.

CONCLUSION

While the science of atmospheric chemistry is advancing rapidly, the several examples of results from current research cited in this paper may serve to demonstrate that there is more to air pollution, and its modeling, than meets the eye.

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TABLE I.- CALCULATED LIMITS FOR DETECTION BY LP-IR SPECTROSCOPY OF SEVERAL
IMPORTANT SPECIES IN PHOTOCHEMICAL SMOG

| Compound | Measurement frequency, cm^{-1} | Absorptivity, ^a α , at 23° C and 760 torr, $\text{cm}^{-1}\text{-atm}^{-1}$ | Resolution, cm^{-1} | Reference | Approximate detection limit at 1-km path, ppb |
|-------------------------------|---|---|------------------------------|-------------|---|
| O ₃ | 1055 | 9.7 | 1 to 2 | 11 and 12 | 10 |
| PAN | 1162 | 32 | 2 to 4 | 13 | 3 |
| NH ₃ | 931 | 27 | 0.5 | Unpublished | 4 |
| | 967.5 | 35 | 0.5 | | 3 |
| | 993 | 21 | 0.5 | | 4 |
| HNO ₃ | 896 | ^b 12 | 0.5 | Unpublished | 6 |
| HCHO | 2779 2781.5 | ^b 16 | 0.5 | Unpublished | 6 |
| HCOOH | 1105 | ^b 70 | 0.5 | Unpublished | 2 |
| HONO | 791 (trans) 853 (cis) | ≈30 71 | 0.5 0.5 | 14 | 10 (cis + trans) |
| H ₂ O ₂ | 1251 | 9 ± 3 | 2 | 9 | 40 |
| HOONO ₂ | 803 | ^b 27 | 0.5 to 1 | 15 | 8 |

^a $\alpha = \ln(I_0/I)/p\ell$ where I_0 is incident intensity, I is transmitted intensity, ℓ is path length (cm), and p is pressure (atm).

^bMeasured from the intensity of the Q branch only.

TABLE II.- POLLUTANT CONCENTRATIONS IN RIVERSIDE AIR, AUGUST 12, 1977, AS
DETERMINED WITH THE FT-IR FACILITY OPERATING AT A PATH LENGTH OF 900 m

| Time | Concentration, ppb, of - | | | | | |
|-------|--------------------------|-----|-----------------|------------------|-------|------|
| | O ₃ | PAN | NH ₃ | HNO ₃ | HCOOH | HCHO |
| 12:00 | 171 | 6 | --- | 14 | 11 | 20 |
| 12:32 | 181 | 7 | 15 | 16 | 10 | 19 |
| 13:02 | 177 | 7 | 33 | 11 | 8 | 16 |
| 13:30 | 195 | 8 | 38 | 9 | 8 | 18 |
| 14:00 | 229 | 7 | 46 | 9 | 9 | 17 |
| 14:30 | 241 | 8 | 32 | --- | 8 | 25 |
| 15:00 | 247 | 11 | 29 | 9 | 6 | 25 |
| 15:30 | 249 | 11 | 32 | 9 | 7 | 22 |
| 15:59 | 211 | 10 | 22 | 9 | 9 | 25 |
| 16:29 | 182 | 4 | 20 | 10 | 5 | 9 |
| 17:03 | 178 | 5 | 13 | 11 | 5 | |
| 17:12 | 182 | 6 | 9 | 10 | 7 | |
| 17:21 | | | | | | 18 |
| 17:31 | | | | | | 20 |
| 17:40 | 156 | 4 | 6 | 8 | 5 | |
| 17:49 | 156 | 7 | 7 | 9 | 6 | |
| 18:01 | | | | | | 21 |
| 18:10 | | | | | | 20 |

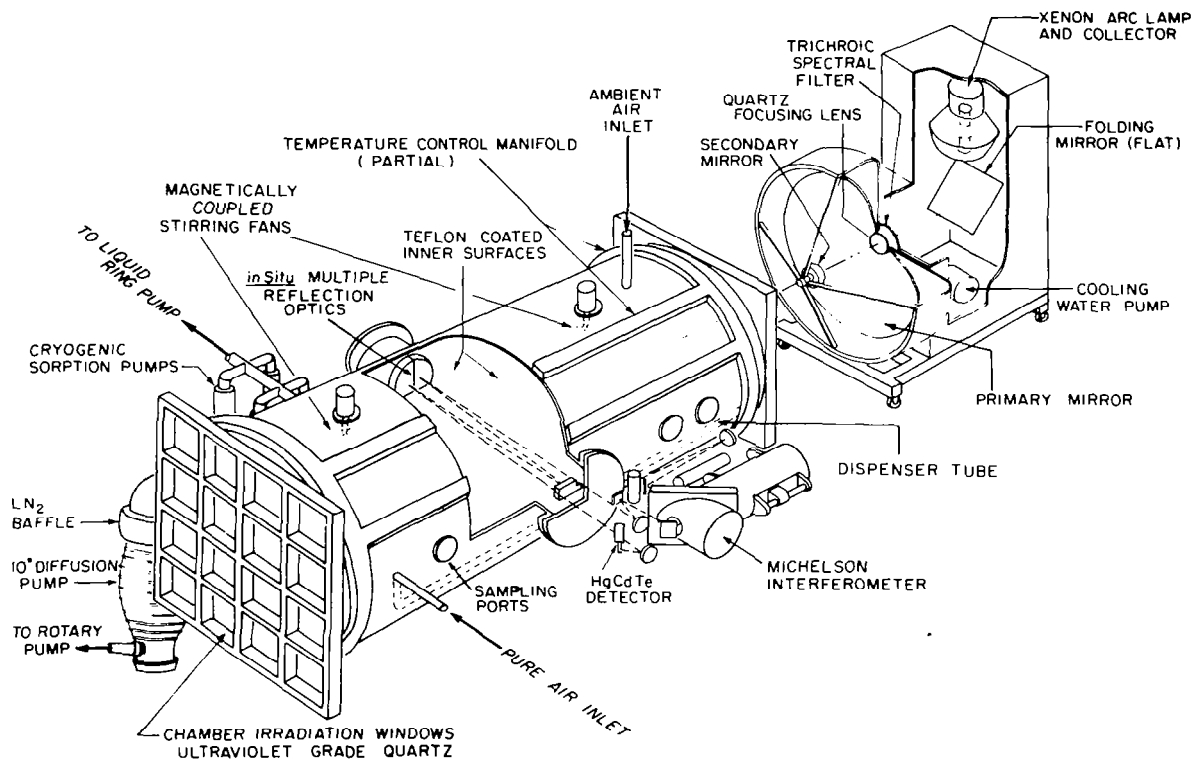


Figure 1.- SAPRC 5800-liter evacuable smog chamber, temperature controlled from -35°C to 100°C , and associated 24-kW solar simulator and Fourier interferometer with long-path infrared optical system.

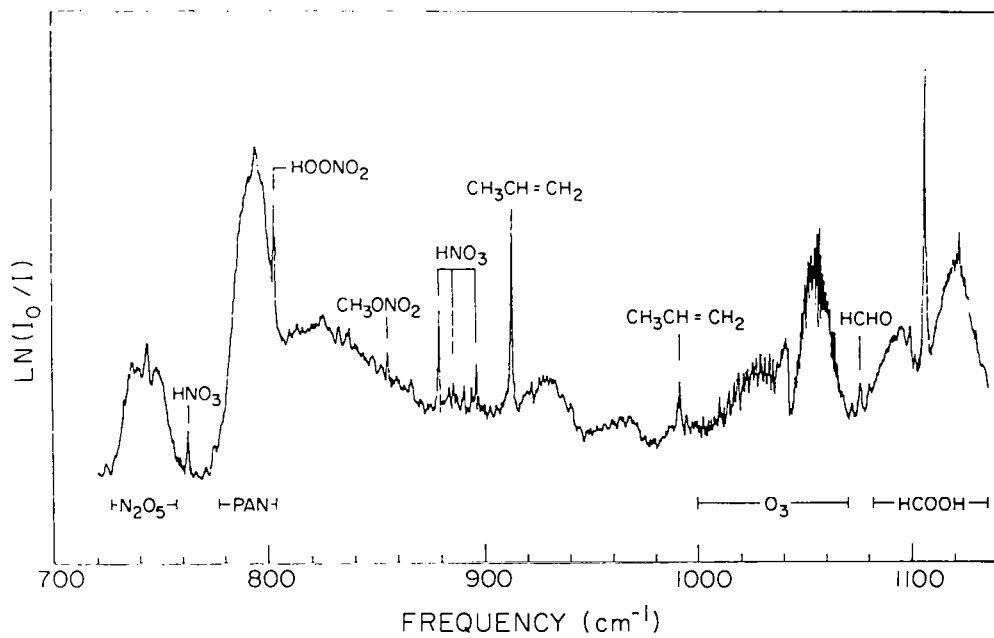


Figure 2.- FT-IR spectrum (absorbance $\text{LN}(I_0/I)$ versus frequency) of products from irradiation of a propylene- NO_x mixture in air at 9.4°C and 85-m path length.

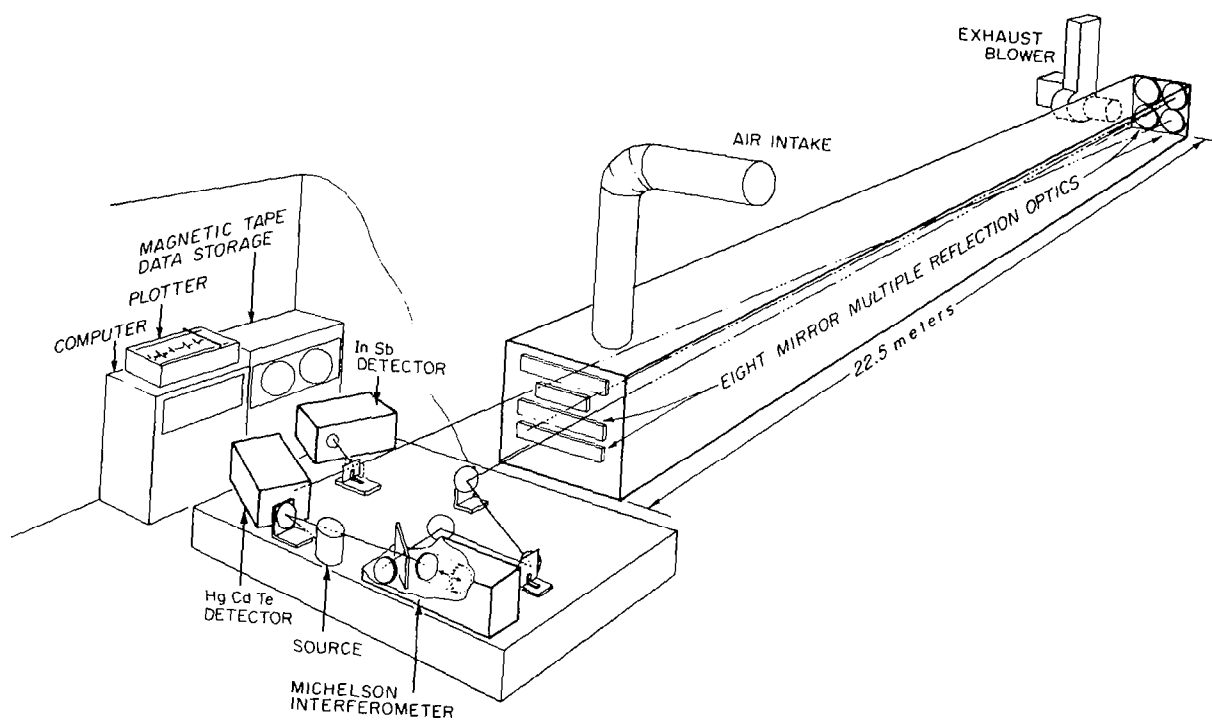


Figure 3.- FT-IR spectrometer and kilometer-path-length multiple-reflection cell used in identifying and measuring trace pollutants in ambient photochemical smog.

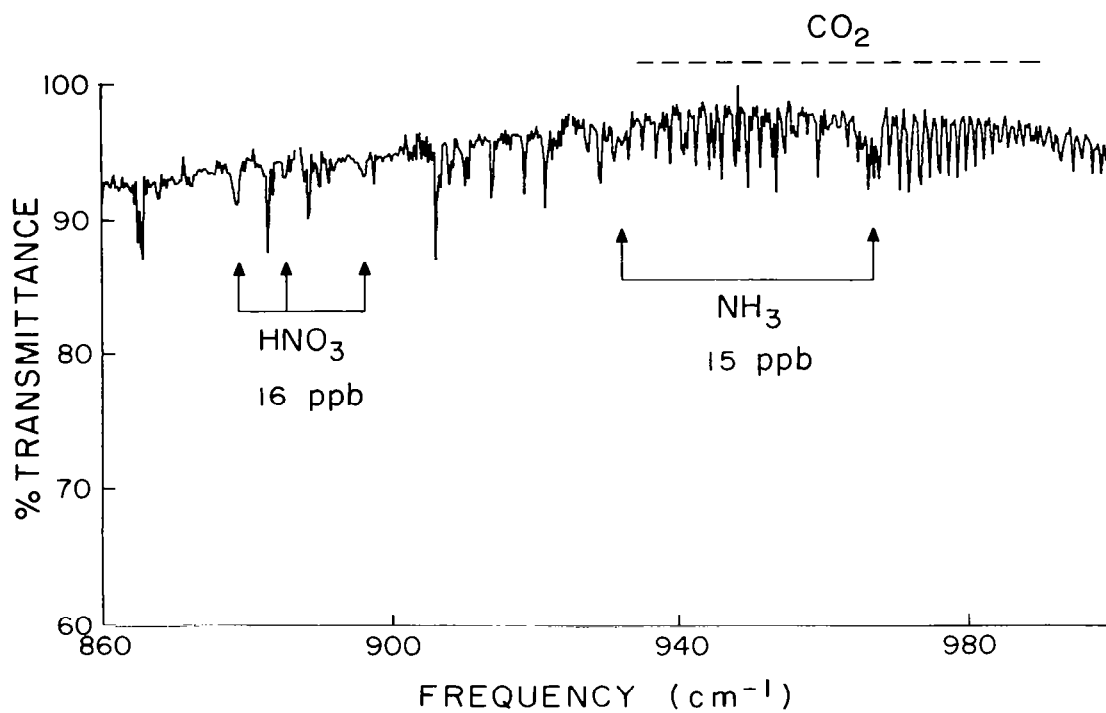


Figure 4.- Riverside ambient air spectrum (August 12, 1977, at 12:32) with 0.5-cm⁻¹ spectral resolution, 900-m path length, HgCdTe detector. Note simultaneous presence of nitric acid and ammonia.

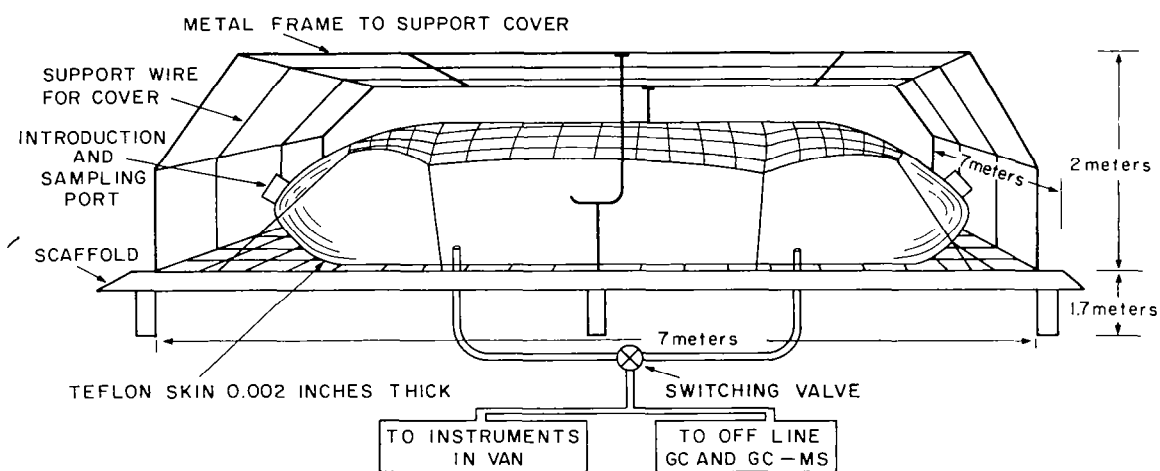
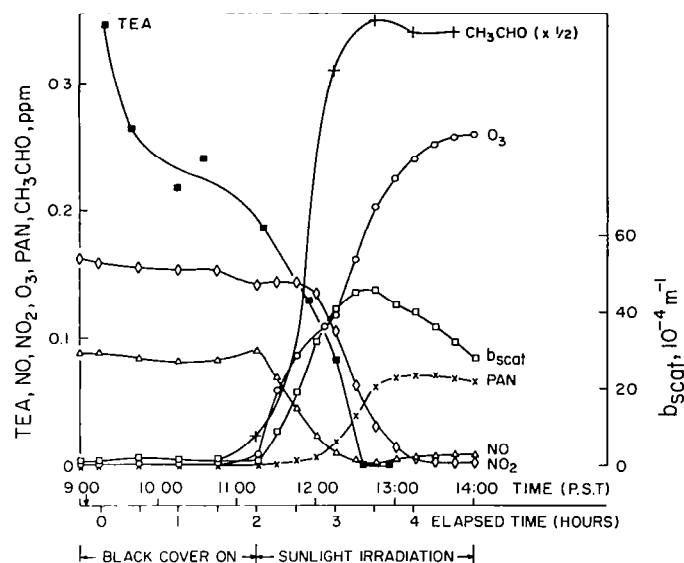
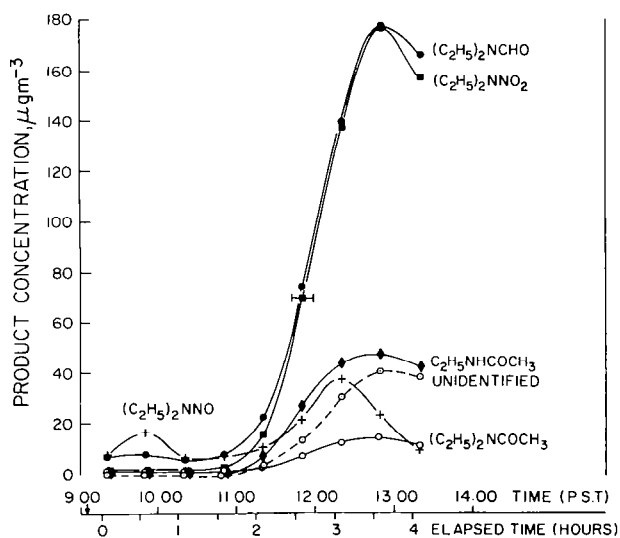


Figure 5.- Outdoor environmental chamber (50 m^3) for the study of the atmospheric reactions of amine- NO_x mixtures in the ppb to ppm concentration range.



(a) Concentrations of TEA, NO, NO₂, O₃, acetaldehyde, and PAN and light scattering coefficient b_{scat} .



(b) Concentrations of diethylformamide, diethylnitramine, ethylacetamide, diethylacetamide, and diethylnitrosamine. Concentration of unidentified compound with molecular weight of 87 was estimated by assuming the same mass spectrometer response factor as diethylacetamide.

Figure 6.- Concentration-time profiles in mixture of triethylamine (TEA) and NO_x on June 23, 1977.